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# FUNDAMENTAL STUDIES OF SEMICONDUCTOR HETEROEPITAXY

## FIRST SEMIANNUAL REPORT

R. P. Rutli

Autonetics Division of North American Rockwell

28 January 1971

United States Army Missile Command AMSMI RND

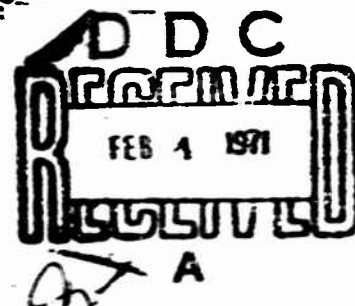
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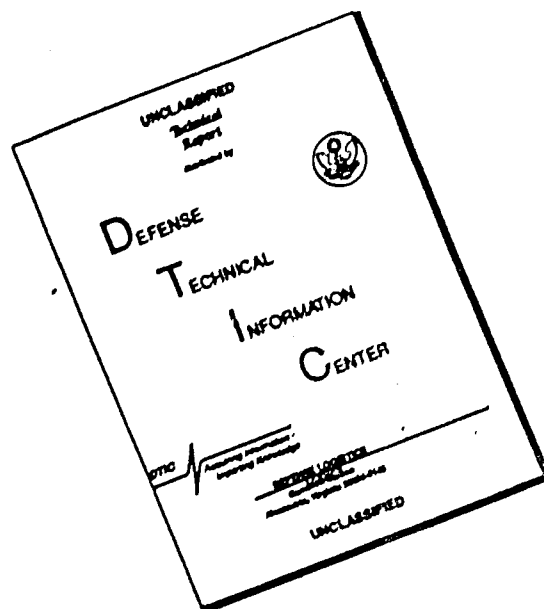
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# **FUNDAMENTAL STUDIES OF SEMICONDUCTOR HETEROEPITAXY FIRST SEMIANNUAL REPORT**

**R. P. Rutli**

**Autonetics Division of North American Rockwell**

**28 January 1971**

**United States Army Missile Command AMSMI RND**

**Redstone Arsenal**

**Huntsville, Alabama**

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## ABSTRACT

The objective of this program is to carry out a fundamental study of the nucleation and film growth mechanisms in heteroepitaxial semiconductor thin films, leading to new understanding of these processes, and to apply the results to the preparation of improved semiconductor thin films and thin-film devices on insulating substrates. The research program involves both theoretical and experimental investigations, divided into nine subtasks -- two theoretical and seven experimental. The emphasis is on chemical vapor deposition (CVD) techniques. The Si-on  $Al_2O_3$  and GaAs-on  $Al_2O_3$  systems are emphasized but other semiconductors and other substrates, such as spinel and beryllia, are to be included.

A generalized theoretical method for the study of crystallographic relationships between substrate and film has been developed, utilizing two-dimensional gaussian distributions of mass as replacements for real atoms on the substrate. The method, which allows pseudomorphic deformation to occur and accounts for the associated elastic strain energy, is applicable either to an extended film or to films of finite extent (i.e., islands), and has been applied to simple square-lattice systems. Another theoretical approach has been utilized in examining effects associated with film-substrate crystallographic relationships, with particular attention to the interfacial cohesive and binding energies between film and substrate. The model under development uses a semi-phenomenological treatment employing a relatively short-range pairwise interatomic interaction potential between Si atoms and the Al and O atoms in and near the interface in the Si- $Al_2O_3$  system. Pseudomorphic distortion is allowed in this treatment, also.

Experimental studies of the effects of various growth parameters and other variables on the quality of Si film growth on  $Al_2O_3$  and spinel substrates have been undertaken utilizing the pyrolysis of  $SiH_4$ . The properties of nominally undoped Si films grown at temperatures less than 1050C are found to be dominated by surface conduction. N-type conductivity, with carrier concentrations from  $\sim 10^{12}$  to  $\sim 7 \times 10^{15} \text{ cm}^{-3}$  and mobilities as high as 700-850  $\text{cm}^2/\text{V-sec}$  are found, but properties vary greatly with surface conditions. Arsenic-doped n-type films with carrier concentrations from  $10^{16}$  to  $>10^{18} \text{ cm}^{-3}$  in both (111) and (100) orientations on  $Al_2O_3$  have been prepared in both  $H_2$  and He at temperatures as low as 950C with good electrical properties. Undoped Si films deposited at temperatures  $>1050\text{C}$  are invariably p-type, due to auto-doping. However, the exact role played by surface conduction is not yet fully evaluated.

Chromatography studies designed to identify the impurities in reactants used in the deposition of Si and GaAs by CVD techniques have been initiated; the investigations are directed toward eventual preparation of reactants of improved purity for use in the program.

Preliminary studies and design of required modifications in an electron microscope to be used for in situ observation of semiconductor CVD are also under way. First experiments involving the observation of some type of film growth in the microscope are expected in the second half of the year.

In addition to the evaluation of deposited films of both Si and GaAs in terms of crystal structure, surface topography, electrical resistivity, carrier concentration and mobility, and optical properties, a novel method of measuring high-field transport properties based on a time-of-flight measurement has been developed.

A detailed outline of the work planned for the second six months of the program is included.

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## SECTION I

### INTRODUCTION

The preparation of thin-film heteroepitaxial semiconductors on insulating substrates for device applications has become a requirement of first-order importance in the semiconductor industry. Many circuits and circuit functions in military electronics now employing solid-state components or low-power vacuum-tube components have potential applications for devices fabricated in heteroepitaxial semiconductors.

Among the many reasons for developing further the techniques for preparing high quality films of heteroepitaxial semiconductors on insulating substrates are the following:

1. Many promising applications for heteroepitaxial Si on insulating substrates have been abandoned or have fallen short of original expectations because of limitations in the quality of the epitaxial layer, resulting at least in part from incomplete understanding of nucleation and early-stage growth phenomena and general inability to take corrective measures to improve this phase of the film growth process.
2. There are applications requiring large-area arrays of devices in which the total cost of fabrication will be less for deposited thin-film devices on an insulating substrate than for the same devices carved out of wafers of bulk crystals.
3. The opportunity to fabricate complete microcircuits in wide-bandgap high-mobility compound semiconductors (such as GaAs) on insulating substrates extends the range of permissible operating temperatures and power levels.
4. The composite structure of a compound semiconductor on a transparent substrate, with controllable bandgaps ranging throughout the spectral range from ultraviolet to long-wave infrared, opens a multitude of potential photodevice possibilities which are impractical with bulk material.
5. Special configurations, such as that of a semiconductor and a piezoelectric material side-by-side on a common substrate, for use in fabricating surface-wave acoustic devices can be routinely achieved by heteroepitaxial growth techniques but are difficult (or in some cases impossible) to obtain utilizing bulk crystals.

An example of a specific instance in which a significant improvement in heteroepitaxial film quality, and thus in device performance, would produce an immediate effect in military electronics applications is the GaAs film-type photocathode recently investigated in a contract program\* at Autonetics. A practical limitation has appeared

\*Fort Belvoir Contract No. DAAK02-69-C-0333, "Heteroepitaxial Deposition of P<sup>++</sup> GaAs on Insulators." (Ref. 1)

on the performance of such a photocathode utilizing heteroepitaxial GaAs on sapphire because of the inferior properties of the GaAs-sapphire interface region. Nucleation and early-stage growth phenomena probably establish this limitation; knowledge of the details of these growth mechanisms could permit improvement in the properties of the interface region and thus in the performance of the device in battlefield surveillance and night vision applications.

Similarly, improvement in the electrical properties of thin heteroepitaxial films of other compound semiconductors on transparent insulating substrates would probably permit fabrication of solid-state infrared vidicon tubes, a military requirement of long standing. In addition, the fabrication of diode and other device arrays as well as discrete thin-film devices and full microcircuits, with emphasis on such important items as microwave mixers and oscillators having significant power handling capability, would probably advance from its present status to full utility as a result of improvements in film properties made possible by knowledge of early-stage growth phenomena.

## 1. PROGRAM OBJECTIVES

The overall objective of this program, for which this is the first Semi-annual Technical Report, is to carry out a fundamental study of the nucleation and film growth mechanisms in heteroepitaxial semiconductor thin films, leading to new knowledge and understanding of these processes, and then to apply these results to the preparation of improved semiconductor thin films and thin-film devices on insulating substrates.

The specific technical objectives of the three-year program are the following:

1. Investigation of various aspects of the mechanisms of heteroepitaxial film growth, to establish (through accumulation of basic knowledge) sets of technical guidelines for the preparation of better films which can then be applied to real situations.
2. Preparation of improved, high-quality, device-grade heteroepitaxial films of Si and GaAs on insulating substrates by chemical vapor deposition (CVD) methods.
3. Development of methods of characterizing heteroepitaxial films as to their suitability for subsequent device fabrication.
4. Design and fabrication of selected thin-film devices which take advantage of the unique properties of such films.

## 2. PROGRAM SCOPE

The program involves both theoretical and experimental investigation of the nucleation and growth mechanisms of heteroepitaxial films in semiconductor-insulator systems, the development of improved techniques for preparation of heteroepitaxial semiconductor films, and the fabrication of some devices utilizing these films, the latter primarily for the purpose of evaluating the heteroepitaxial film materials but also to exploit the special properties of the films.

The theoretical studies in the program are of two types. First, there is "on-line" response to the needs of the experimental program involving data analyses, theories and explanations, and guidance in identifying definitive experiments. Second, original exploration of theoretical topics of fundamental importance to the field of epitaxy, perhaps only indirectly related to the experimental problems of the moment, will continue throughout the program; the goal of such theoretical studies will be the generation of significant theoretical advances in the field of heteroepitaxy.

The experimental investigations are also of two types. First, fundamental explorations are being undertaken to elucidate mechanisms and general principles of the heteroepitaxial growth process. Second, practical studies accompany the fundamental investigations so that useful discoveries and developments can be immediately applied to improvement of the properties of the semiconductor films, which can then be utilized in fabricating the experimental devices.

CVD methods are the most common and successful in use for film growth in the semiconductor industry, and it appears that this circumstance will continue for some time. Consequently, the emphasis in this program is on such techniques. Most previous fundamental studies of epitaxy have concentrated upon physical vapor deposition (PVD) methods, partly because both experimental and theoretical scrutiny are easier with these techniques. However, they will be employed in this program only at those times when they will be clearly helpful in the search for understanding.

Si and GaAs are to be used for most of the work, together with substrates of sapphire ( $\text{Al}_2\text{O}_3$ ), spinel (both stoichiometric and nonstoichiometric), and beryllia ( $\text{BeO}$ ). Si and GaAs have been chosen because of the preeminence of the former in the semiconductor industry and the high-frequency and high-temperature attributes of the latter; in addition, they represent the elemental and compound semiconductors for which most comparative information exists.

Si-on- $\text{Al}_2\text{O}_3$  and GaAs-on- $\text{Al}_2\text{O}_3$  are the semiconductor-insulator systems to be emphasized, based in part on the success already achieved with these systems (albeit in the absence of full fundamental understanding) and in part on the potential value of these systems to device technology. However, if it becomes advisable as the program develops, other semiconductor-insulator combinations will be brought into consideration, employing either CVD or PVD.

### 3. PROGRAM DESCRIPTION BY SUBTASK

To carry out the overall program task, the research has been divided into nine subtasks as follows:

#### a. Theoretical Studies

##### (1) Subtask 1

Theoretical examination of CVD kinetics and the processes of nucleation, surface migration, and film growth with emphasis on crystallographic relationships between overgrowth and substrate, using both "classical" and recently developed techniques and concepts, to attempt to identify mechanisms and establish general principles of heteroepitaxial growth.

(2) Subtask 2

Calculation of interfacial (surface) binding energies and other parameters involving the quantum mechanics of surfaces and interfaces, based primarily on the pseudopotential approach, which could add significantly to the present knowledge of binding energies and the heteroepitaxial process.

b. Experimental Studies

(1) Subtask 3

Investigation of the delivery kinetics of CVD processes, to improve the detailed understanding and control of the chemical reactions involved in the preparation of heteroepitaxial semiconductor films by CVD; also preparation of films for use in other parts of the program.

(2) Subtask 4

Analysis and purification of reactant materials used in metal-organic-hydride and other CVD processes, and preparation of sample quantities of improved-purity reactants so that films of higher quality can be obtained.

(3) Subtask 5

Preparation of substrates and characterization of surfaces and impurity content of substrates for use in semiconductor heteroepitaxy, with particular attention to such factors as surface orientation, defect structures, and surface purity.

(4) Subtask 6

Correlation of properties of grown heteroepitaxial semiconductor films with measured substrate properties and CVD process parameters, and explicit experimental verification of these correlations.

(5) Subtask 7

In situ observation and study of the early stages of growth of CVD films in the electron microscope, to develop additional fundamental knowledge of the epitaxy process. Results of these experimental observations will be incorporated into theoretical studies as they become available.

(6) Subtask 8

Measurement of the electrical, optical, crystallographic, and thermal properties of heteroepitaxial semiconductor films on insulators by a variety of measurement techniques. Standard techniques will be employed and new methods developed where required for measurement of those film properties which appear best to characterize ultimate device performance.

(7) Subtask 9

Design and fabrication of certain types of devices, using some of the heteroepitaxial films produced in the above studies. Some devices will be used to evaluate material properties and others to exploit semiconductor film characteristics unique to heteroepitaxial systems.

Additional specific subtasks may be added to the program as the work progresses, consistent with the status of the program work at the time or in response to specific requests by the contract monitor.

## SECTION II

### RESULTS AND DISCUSSION

The progress achieved during the first six months of the program is summarized in this section. All of the subtasks (see preceding section) are technically under way, although two of them (Subtask 8 -- correlation of film properties with substrate properties and CVD process parameters -- and Subtask 9 -- design and fabrication of devices in improved films) will not be fully activated until later in the program.

A summary of the progress on the other subtasks follows.

#### 1. THEORETICAL STUDIES

In addition to the "on-line" interactions with experimentalists, which are planned as an important and integral part of the theoretical effort on this program, the activities of the theoreticians associated with the contract have now become clearly defined and directed toward the solution of several specific problems in the field of semiconductor heteroepitaxy. This work will be discussed in some detail here.

##### a. Subtask 1: Classical Epitaxy Theory -- Nucleation, Kinetics, Crystallographic Relationships

Considerable work has been done on the development of a generalized theoretical method for the study of crystallographic relationships between substrate and film. Among the important factors to be considered in such an investigation are the following:

1. Imperfection of substrate surface
2. Deformation of substrate surface in presence of film overgrowth
3. Precise nature of interface potential between film and substrate
4. Strain energy as function of orientation
5. Registry by pseudomorphic deformation or by dislocations at the interface
6. Surface free energy of exposed facets of islands
7. Extent of overgrowth -- i. e., extended film or separate islands.

The generalized method adopted is a semi-empirical means for describing the coordinated effect of factors 1, 4, 5, and 7, with possible later consideration of 6. Factor 3 would have to be parameterized and determined, among a limited number of possibilities, by fitting experimental data or through use of semi-empirical interatomic force curves, such as Morse curves. Restrictions such as the symmetry and periodicity of lattices, the known state of imperfection of substrates, relative surface energies, and known elastic coefficients do, however, limit the empirical alternatives so that a rational deduction of realistic growth and orientation mechanisms should be achievable.

Although completely accurate predictions of growth behavior in particular cases will remain out of reach, enough guidelines can be established by these methods to indicate probable ranges of specific results. The method used is briefly described in the following paragraphs.

If an individual free overgrowth atom migrates on the exposed substrate surface, it will experience a potential (usually periodic, except for perturbations due to defects) which will be denoted by  $U_p(\bar{r})$ , where  $\bar{r}$  is the position vector on the substrate surface. For reasons of achieving convergence in an analytical representation of the interface potential for a film of such atoms, it is convenient to replace the usual "point" atom with a two-dimensional gaussian distribution of mass which has the same total interaction with the substrate as does the real or "point" atom. The mass in such a "gaussian" atom is distributed about a center located at  $\bar{r} = \bar{r}_0$  as follows:

$$\rho_g(\bar{r}-\bar{r}_0) = \frac{1}{\pi n^2} e^{-\frac{(\bar{r}-\bar{r}_0)^2}{n^2}}, \quad (1)$$

where  $\rho_g$  is the mass density and  $n$  measures the "width" of the gaussian atom. Thus, the gaussian atom becomes a point atom of unit mass when  $n \rightarrow 0$ .

An interaction potential  $\phi$  per unit mass is chosen such that

$$U_g(\bar{r}) = \int \phi(\bar{r}_0) \rho_g(\bar{r}-\bar{r}_0) d\bar{r}_0, \quad (2)$$

where  $U_g(\bar{r})$  is the total potential experienced by the gaussian atom. For example, consider that  $U_p(\bar{r})$  is given by

$$U_p(\bar{r}) = A \left( 1 - \cos \frac{2\pi x}{b} \cos \frac{2\pi y}{b} \right), \quad (3)$$

in which  $A$  and  $b$  are constants and  $x$  and  $y$  are the components of  $\bar{r}$ , i.e.,  $\bar{r} = \bar{i}x + \bar{j}y$ .

The potential corresponds to a substrate having a primitive square lattice of parameter  $b/\sqrt{2}$  rotated at an angle of 45 degrees to the  $x$ -direction. Potential minima occur over substrate atoms. In terms of a nonprimitive unit cell, the lattice is a face-centered square lattice of parameter  $b$  parallel to the  $x$ -direction. Either of these descriptions is satisfactory. If  $\phi(\bar{r}_0)$  is chosen as

$$\phi(\bar{r}_0) = \alpha - \beta \cos \frac{2\pi x_0}{b} \cos \frac{2\pi y_0}{b}, \quad (4)$$

then Equations (1) and (2) require that

$$U_g(\bar{r}) = \alpha - \beta e^{-\pi^2 n^2/b^2} \cos \frac{2\pi x}{b} \cos \frac{2\pi y}{b}. \quad (5)$$

To ensure that the point atom potential  $U_p(\vec{r})$  and the gaussian atom potential  $U_g(\vec{r})$  are equivalent it is necessary that

$$\alpha = A$$

and

$$\beta = Ae^{\pi^2 n^2 / b^2} \quad (6)$$

The potential of the entire film is next considered. In order to obtain an analytical expression for the film potential it is first necessary to find an expression for the distributed mass density in a periodic film constructed of gaussian atoms. This density may be written as

$$\rho_f(\vec{r}) = \sum_i \rho_g^{(i)}(\vec{r} - \vec{r}_i), \quad (7)$$

where  $\rho_g^{(i)}$  refers to the  $i$ th gaussian atom centered at  $\vec{r}_i$  in the film. Because of the periodic nature of the extended film it is possible to expand  $\rho_f$  in a Fourier series whose coefficients are indexed in the reciprocal lattice of the film.

First, however, an internal coordinate system rigidly fixed in the film must be introduced. The position vector in this system is  $\vec{s} = \vec{i}'u + \vec{j}'v$ , where  $\vec{i}'$  and  $\vec{j}'$  are unit vectors fixed in the film, and  $u$  and  $v$  are the corresponding components of  $\vec{s}$ . The transformation between  $\vec{s}$  and  $\vec{r}$  is

$$x = u \cos \theta - v \sin \theta,$$

and

$$y = u \sin \theta + v \cos \theta, \quad (8)$$

where  $\theta$  is the angle of rotation of the film coordinate system with respect to that of the substrate.

It now follows that

$$\rho_f(\vec{s}) = \sum_{\vec{h}} \rho_{\vec{h}} e^{-i2\pi\vec{h}\cdot\vec{s}}, \quad (9)$$

where  $\vec{h}$  is a reciprocal vector and  $\rho_{\vec{h}}$  are the Fourier coefficients. Since  $\rho_f(\vec{s})$  can be expressed as

$$\rho_f(\vec{s}) = \sum_i \rho_g^{(i)}(\vec{s} - \vec{s}_i), \quad (10)$$

it follows that  $\rho_{\vec{h}}$  can be calculated in a straightforward manner. For example, if the film consists of a simple square lattice of parameter  $a$  with a gaussian atom centered at each node point, it can be shown that



$$\rho_f(\vec{r}) = \frac{1}{a^2} \left\{ 1 + \sum_{l=-\infty}^{\infty} e^{-\frac{2\pi^2 l^2}{a^2}} \cos \frac{2\pi l x}{a} + \sum_{m=-\infty}^{\infty} e^{-\frac{2\pi^2 m^2}{a^2}} \cos \frac{2\pi m y}{a} + \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} e^{-\frac{2\pi^2 (l^2 + m^2)}{a^2}} \cos \frac{2\pi l x}{a} \cos \frac{2\pi m y}{a} \right\} \quad (11)$$

In this equation  $l$  and  $m$  are integers, and the primes on the summation signs indicate that the terms  $l = 0$  and  $m = 0$  are omitted. As given above,  $\rho_f(\vec{r})$  is strictly correct only for a film of infinite extent since it involves an expansion in terms of reciprocal lattice vectors. The application of Equation (11) to finite films will therefore be an approximation. First, the mass distributions of individual gaussian atoms are required to be sensibly nonoverlapping; therefore the gaussian width parameter  $a$  is chosen to be  $\approx a/6$ . Second,  $\rho_f(\vec{r})$  is set equal to zero whenever the position vector  $\vec{r}$  lies outside of the finite film being treated. For example, for a square island of film having  $(2p+1)$  atoms on a side and length  $2L = a(2p+1)$ ,  $\rho_f(\vec{r})$  is zero whenever

$$|x| \geq L + \frac{a}{2} \quad (12)$$

and

$$|y| \geq L + \frac{a}{2}.$$

When this is done, Equation (11) can be used to approximately describe finite films. Thus, for a finite film the density can be expressed as

$$\rho'_f(\vec{r}) = H(x, L) H(y, L) \rho_f(\vec{r}), \quad (13)$$

where the  $H$  functions are zero whenever the conditions of Equation (12) hold.

The various series in Equation (11) converge fairly rapidly for finite  $a = a/6$ ; this indicates one reason for using gaussian atoms. However, caution must be exercised and the convergence determined only after the convolution of  $\rho'_f$  with  $\phi$ , since there are constructive interferences between the periodic density distribution and the periodic potential which persist to very high orders. The total finite film

potential  $U_f$  may now be expressed solely in terms of the lattice parameter  $a$  and the angle of rotation  $\theta$  by

$$U_f(a, \theta) = \int \phi(\bar{r}) \rho_f(\bar{s}) d\bar{s}. \quad (14)$$

Equation (8) must be used to express the position vector  $\bar{r}$ , in  $\phi(\bar{r})$  above, in terms of  $\bar{s}$  before the integration in Equation (14) is performed.

It is assumed in all of the above that the central atom of the island lies directly over a substrate atom. Translational effects can, however, be treated by removing this limiting assumption.

For small islands, and even for some extended films, there is experimental evidence that pseudomorphic deformation rather than dislocation generation is the mechanism for minimizing the combined elastic and interface energies. When this is the case, the increased negative binding energy associated with the pseudomorphic deformation more than compensates for the positive elastic energy due to the deformation, and thus a lower total energy is obtained.

If the natural lattice parameter of the film is  $a_0$ , the strain energy in the equilibrium configuration can be approximated by

$$V(a) = \Gamma(a - a_0)^2, \quad (15)$$

where  $\Gamma$  is a modulus depending on the elastic coefficients. The total energy will then be

$$E(a, \theta) = V(a) + U_f(a, \theta). \quad (16)$$

Experimentally observed crystallographic orientations of film and substrate will correspond to configurations of minimum total energy. Within the framework of the present model, these configurations can be determined by minimizing  $E(a, \theta)$  in the above equation with respect to  $a$  and  $\theta$ .

The validity of this model and the above analysis has been established for the limiting case of an extended film, where  $L \rightarrow \infty$  and  $E(a, \theta)/N$  is the energy per atom. For simplicity, it was further assumed that  $\Gamma \rightarrow 0$ , i.e., no elastic energy. Non-zero values of the binding energy per atom  $U_f(a, \theta)/N$  are obtained only when the geometrical conditions of either Equation (17a) or Equation (17b) are satisfied:

$$\cos \theta = \sin \theta = \frac{1}{\sqrt{2}} \quad \text{and} \quad a = b/\sqrt{2}. \quad (17a)$$

$$\left(\frac{m+l}{2}\right) \frac{b}{a} = -\sin \theta \quad \text{and} \quad \left(\frac{m-l}{2}\right) \frac{b}{a} = \cos \theta. \quad (17b)$$

Equation (17a) represents the simplest case, that of autoepitaxy, while Equation (17b) identifies all of the crystallographic relationships involving commensurability between overgrowth and substrate for the more general case. Thus, physically correct results have been obtained from the gaussian atom model for these cases.

For films of finite extent the appropriate expressions can be made to converge rapidly by choosing the gaussian width parameter  $n$  as large as  $a/8$ . In this way, the finite film case becomes tractable; the accuracy of the method has been checked for the simple case of small angles of rotation  $\theta$ .

The method described here is now being applied to real film-substrate systems.

#### b. Subtask 2: Theoretical Studies of the Quantum Mechanics of Surfaces

The results obtained in experimental heteroepitaxy are known to be dependent upon a number of variables and experimental conditions, including source material impurities, substrate preparation methods and perfection; (including both intrinsic defects and extrinsic defects such as surface impurity atom complexes), and substrate crystallographic orientation.

The relation of orientation and crystallographic direction to heteroepitaxial film quality is likely to involve both "direct" and "indirect" effects. The direct effects can be defined as those associated with particular film-substrate crystallographic orientation relationships for a substantially ideal film (i.e., with bulk crystal qualities) on a substantially ideal (bulk-crystal) substrate. Indirect effects, on the other hand, can arise if different growth and/or deposition planes behave differently with respect to the formation of surface impurity complexes, surface catalysis of chemical reactions, or some impurity- or defect-induced nucleation. In the theoretical investigations described in the present section the so-called direct effects relating to bulk or slightly modified bulk film-substrate crystallographic relationships are considered.

The work on this subtask began late in the fourth month of the contract program and increased to the planned level of effort in the sixth; the major theoretical effort in the first year will take place in the second six months. The principal activity has been the investigation of theories and theoretical approaches to the problems of cohesion and structure as applied to heteroepitaxy. The three theoretical problems of the direct-effect nature believed to be most relevant to the experimental heteroepitaxy investigations are: (1) the interfacial cohesive and binding energy between film and substrate, (2) the interfacial-state energy bands and associated electronic conductivity, and (3) the film surface-state energy bands and associated electronic conductivity. The first of these three problems has received the most attention to date.

Before a more detailed discussion of this investigation is undertaken, the question of why the binding energy between film and substrate is of importance in heteroepitaxy will be examined briefly. The simplest analysis of the physical "compatibility" of a film-substrate combination is a geometrical consideration of the "fit" or "match" between atoms of various crystallographic planes in the film and substrate lattices. However, such a geometrical model has proven of little value in that film-substrate systems with small mismatch do not always lend themselves to successful epitaxy, while some systems with a large mismatch result in good epitaxial growth. The logical next step in understanding the basic principles of heteroepitaxy is to attempt to determine the actual film-substrate interfacial binding energies for planes

of various orientations of a given film-substrate system. Any progress on this problem and any guidelines which can be evolved could be of real importance in the practical applications of heteroepitaxy.

In the theoretical studies thus far, the attempt has been made to develop a method of calculation of interfacial binding energy between film and substrate which is more realistic (and therefore useful) than other previous calculations of this kind. Prior work presently accessible in the literature is far too idealized to allow determination of any distinguishing characteristics between various film-substrate orientations in a system such as Si-on- $\text{Al}_2\text{O}_3$ .

To the extent possible, the binding-energy calculational model should be based on solid-state quantum mechanics. The original intent was to perform a Green's function/Wannier-basis calculation of the one-electron redistribution energy of the interface. This redistribution energy is, in the present terminology, the effective binding energy. Further investigation of this approach, which would be an explicitly quantum-mechanical treatment utilizing first principles, led to the conclusion that such a procedure is not feasible within the time scale and available level of effort of the total contract program. In addition, the approach has two features which now appear important as disadvantages. First, this method makes use of and tends to focus attention on basis functions (explicitly the localized Wannier functions, but implicitly the usual Bloch functions). A simpler alternative approach, which does not require laborious calculation of Bloch functions per se, would be desirable. Second, it is considered important to include the elastic energy due to structural deformation near the interface. It has not been possible to incorporate such deformation into the Green's function/Wannier-basis technique without badly complicating an already difficult problem.

These difficulties have required that a rather different approach be taken to the calculation of interfacial binding energies. The model presently being developed is a semi-phenomenological treatment which employs a relatively short-range pairwise interatomic interaction potential between Si atoms and the Al-O atoms lying in and near the interface. Provided the interatomic potentials can be determined and are found to be of relatively short range, the binding energy can be calculated with computers. The relative orientations of the interfacial film-substrate planes can then be varied, and in this way the orientation dependence of the binding energy can be determined.

The actual total energy will, however, include elastic contributions due to the relaxation from the "ideal" bulk configuration into an atomic configuration with greater (negative) binding energy at the expense of elastic (positive) energy. It is not now feasible to determine the actual relaxed equilibrium location of all atoms. To do this would involve the independent virtual displacement of all those atoms partaking in relaxation, and calculation of binding energy for each configuration. This is outside of present computer feasibility. In the interest of practicality, a pseudomorphic distortion or strain will be employed which is maximum near the interface and dies off toward the free surface of the film according to classical elasticity theory.

The major uncertainty which must be resolved within this calculation is the forms and values taken on by the interatomic potentials. Recent work (Ref 2) on cohesion and structure suggests that it may be possible to determine reasonable potentials from the pseudopotential formulation of the "band structure energy". In

the cited work it is shown that the k-space "band structure energy" can (in principle) be Fourier-transformed into real physical space to yield an interatomic potential. At any rate, the determination of reasonable potentials is presently being attempted by this method.

The calculation of binding energies as discussed here uses a semi-empirical pairwise interatomic interaction potential. The binding energy is also being calculated as part of Subtask 1 (see preceding section), using a different type of potential. The bulk of that work has employed a potential which is two-dimensional and depends only upon position in the interfacial plane, as indicated earlier. The third dimension, i. e., displacement normal to the plane, is not explicitly included. Thus, the potential used in those calculations is not as fundamental and may not be as realistic, *a priori*. The approach being used in Subtask 1, however, does possess the strong advantage that the simpler potential allows a more complete analytical solution before resorting to numerical solution. Thus, qualitative features can be more readily determined.

On the other hand, the advantage of the three-dimensional potential, with a summation over all atoms rather than over all lattice sites in an interfacial plane, should lie in the more realistic numerical results, although qualitative features may not be so readily determined and presented. One further advantage is that it may become possible to determine to what extent the summation of three-dimensional potentials over all atoms near the interface can actually be represented by an effective two-dimensional potential. There are thus common aspects of both theoretical efforts; where appropriate, theoretical investigations are being pursued jointly.

## 2. EXPERIMENTAL STUDIES

The experimental studies constitute the major part of the contract effort. Although two of the subtasks (6 and 9) are not fully under way, most of the experimental program is in progress and is reviewed in this section.

### a. Subtask 3: CVD Delivery, Kinetics and Film Preparation

In the first year of the program it is intended that both the Si-on-insulator and the GaAs-on-insulator systems be investigated, with attention directed toward identifying the following in both systems:

1. Preferred substrate
2. Optimum growth temperature
3. Preferred film orientation
4. Preferred growth atmosphere
5. Preferred substrate orientation
6. Optimized over-all growth process.

During the first six months of the program, studies of the effects of various growth parameters and other variables on the quality of Si films grown on  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$  substrates were undertaken. Particular attention was paid to growth on

$Al_2O_3$ , for this substrate has a rhombohedral crystal structure (Si is diamond-cubic) and could, therefore, provide epitaxial growth data potentially valuable to the theoretician's attempts to model heteroepitaxy. Since  $MgAl_2O_4$  is a cubic material, like Si, it is less attractive as a host for Si in basic studies of heteroepitaxy because completely parallel orientation relationships (i.e., (111) Si/(111)  $MgAl_2O_4$ , etc.) have been observed in the Si- $MgAl_2O_4$  system. In the GaAs- $MgAl_2O_4$  system, however, explaining the (100)GaAs growth experimentally observed on (110)  $MgAl_2O_4$  is a challenge to the theoretician.

On the other hand, considerable interest has been generated in  $MgAl_2O_4$  as a possible preferred substrate for Si growth, based primarily on a comparison of the electrical properties of (100)Si growth on (0112) $Al_2O_3$  with those of (111)Si growth on (111) $MgAl_2O_4$ . However, it is significant to note that high quality (111)Si growth has also been reported on (0001) $Al_2O_3$ . (Ref 3)

Since one of the objectives of this program is the preparation of high-quality Si films on insulating substrates, comparative Si growth data on  $Al_2O_3$  and  $MgAl_2O_4$  are now being accumulated and evaluated. These studies will lead to a realistic determination of the preferred substrate for heteroepitaxial Si, based on such criteria as growth temperature, film orientation, growth atmosphere, and substrate surface quality and orientation. There are several different orientations of  $Al_2O_3$  that promote (111)Si growth; differences that are observed in the growth parameters which promote high quality (111)Si growth in these several cases should, therefore, be related to the condition of the substrate surface, its orientation, and its chemical behavior in the CVD environment. Such differences could be of considerable importance to the theoretician.

The initial growth studies in this program involved the formation of Si films by the pyrolysis of  $SiH_4$  (Matheson Co.) in the apparatus depicted in Figure 1. It consists principally of a single vertical 60 mm-OD quartz (standard grade) tube 38 cm long, containing a SiC-covered carbon pedestal ("Ti-Kote", Texas Instruments) which can be inductively heated and rotated; a manifold made from 1/4 in.-OD stainless steel (type 316) tubing; appropriate flowmeters (Brooks Instruments Co.) for monitoring the gas flows; a teflon connector (Beckman Instruments) to facilitate reactor exchange; and provision for separate evacuation of the flow lines and the reactor. During the working day a continual flow is maintained in the gas lines; only the reactor portion and connections are evacuated between experiments. The  $H_2$  carrier gas is Pd-purified, and the He is grade 5TM from Airco. The dopant source presently in use contains 200 ppm AsH<sub>3</sub> in a  $H_2$  carrier gas (Matheson Co.). Temperatures of the SiC-coated C pedestal are measured with an optical pyrometer and are uncorrected for apparent emissivity changes caused by the intervening quartz wall.

Undoped Si films were used in the first work in the expectation that the electrical properties of such films would be more sensitive to changes in CVD deposition parameters, substrate conditions, and other controllable factors. However, it was determined that the properties of undoped Si films grown at temperatures less than 1050 C are dominated by surface conduction (see Subtask 8). It appeared expedient to add an n-type dopant, in this case As, to the growing film and to establish conditions for the growth of films with donor carrier concentrations from  $10^{16}$  to  $> 10^{18} \text{ cm}^{-3}$ , so that the effects of the Si surface might be minimized.

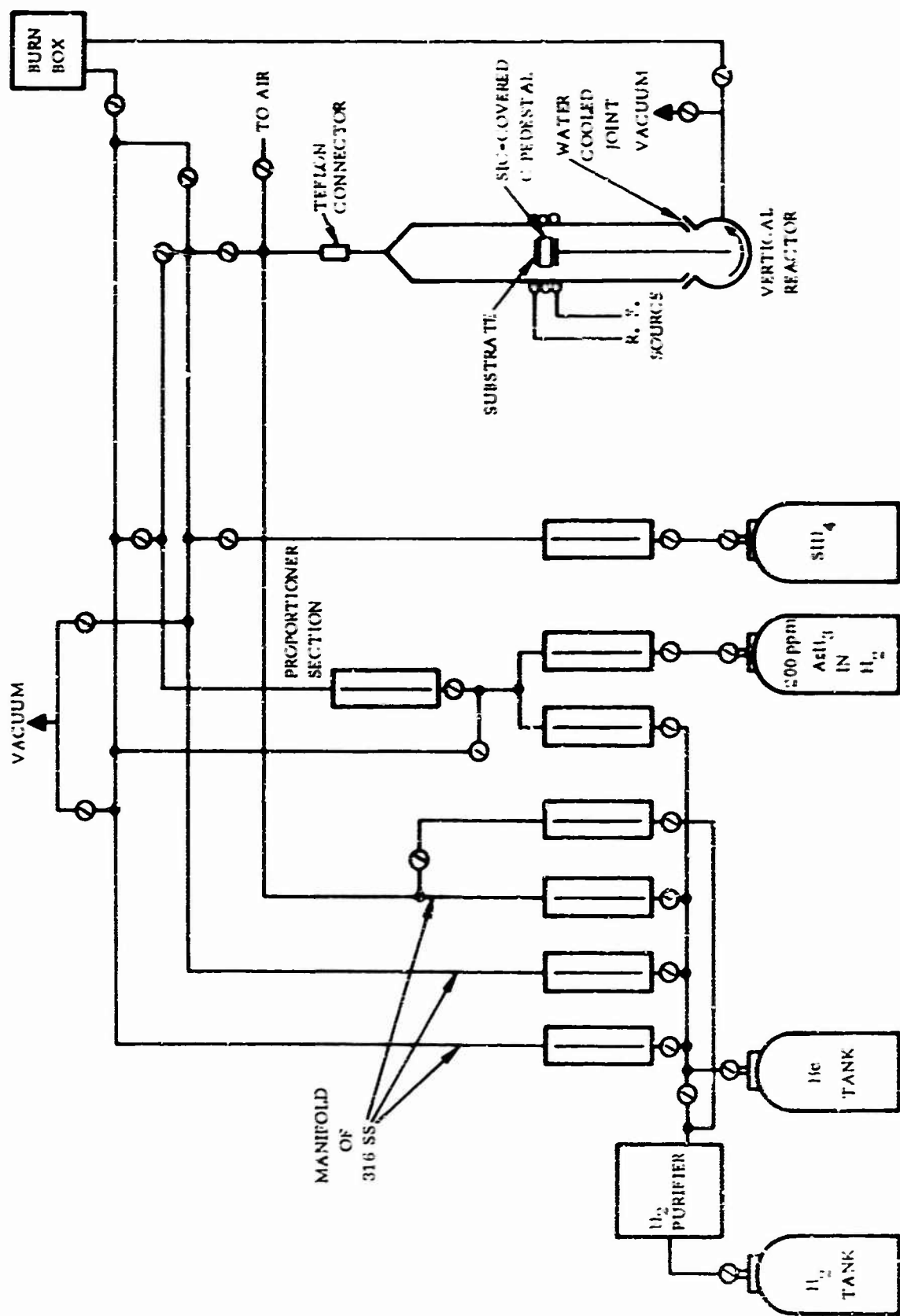


Figure 1. Schematic Diagram of Chemical Vapor Deposition Apparatus



The electrical results obtained on such films to date (Subtask 8) verify the achievement of good quality n-type (111) Si and (100) Si growth on  $Al_2O_3$  at growth temperatures as low as 950 C. In a He atmosphere, (100)Si epitaxy was obtained as low as 800 C, but the films were relatively poor in appearance. These results are discussed further in Section III.

He may be preferred over  $H_2$  as the carrier gas if autodoping of the Si film is to be minimized. The high temperature etching of  $Al_2O_3$  by  $H_2$  was first reported in 1963 (Ref 4) as an experimental step useful for "preparing" an  $Al_2O_3$  surface for Si epitaxy. A plausible reaction for explaining  $Al_2O_3$  removal is indicated by Equation (18):



It was also reported in 1963 (Ref 4) that a second reaction was important at these temperatures:



Both reactions release Al compounds into the growth environment in the early growth stages until Si coverage of the substrate surface is attained and also during subsequent Si film growth from areas not covered by Si (such as the back of the substrate wafer). Therefore, Si growth at such temperatures and in such environments that minimize or eliminate the effects of the reactions of Equations (18) and (19) is desirable. An inert atmosphere (e.g., He) solves the problem represented by the reaction of Equation (18), and low temperatures overcome the difficulty introduced by the reaction of Equation (19).

The experiments carried out so far have indicated that at temperatures > 1050C nominally undoped Si films grown in  $H_2$  were invariably p-type (as determined with a hot-probe), n-type when grown at 1000 C, and sometimes both n- and p-type in adjoining areas when grown at ~1050C. However, it was also observed that hot-probe typing lead to the same results for films grown in a He atmosphere, a rather surprising result which might be explained if the reaction of Equation (19) were more important than that of Equation (18) in the autodoping process. The effect on autodoping of the  $H_2$  produced during  $SiH_4$  decomposition,



has not yet been assessed. (The reaction expressed in Equation (20) is oversimplified, since decomposition of  $SiH_4$  in a He atmosphere was observed to produce a yellow film on the reactor walls, presumably a Si hydride, which could be decomposed to yield Si and  $H_2$ . Heavy yellow deposits of this nature sparked when contacted by acid mixtures.)

The above considerations indicated that the preferred growth temperature range for further studies in Si heteroepitaxy on  $Al_2O_3$  was 950-1050 C to provide high quality (100)- and (111)-oriented Si films essentially uncompensated by Al. These temperatures were also found to be usable for Si growth on (111)-oriented Czochralski-grown  $MgAl_2O_4$ .



One of the criteria which have been advanced for favoring  $\text{MgAl}_2\text{O}_4$  over  $\text{Al}_2\text{O}_3$  as a substrate is that the thermal expansion coefficient for  $\text{MgAl}_2\text{O}_4$  is less than that for (01 $\bar{1}$ 2)  $\text{Al}_2\text{O}_3$ . However, the thermal expansion for  $\text{Al}_2\text{O}_3$  is orientation dependent, and various orientations of  $\text{Al}_2\text{O}_3$  have thermal expansion coefficients lower than that of  $\text{MgAl}_2\text{O}_4$  and closer to the value for Si. Results of initial growth experiments on such orientations of  $\text{Al}_2\text{O}_3$  (based only upon general film appearance at this point) have been quite encouraging, and studies are continuing in the preparation and evaluation of films grown on these orientations.

#### b. Subtask 4: Analysis and Purification of CVD Reactants

Review of available literature has shown that silane ( $\text{SiH}_4$ ) and its suspected contaminants can be safely handled and separated on gas chromatograph columns containing deactivated solid supports coated with nonpolar liquid phases, e.g., AW-DMCS Chromosorb P coated with Silicone Oil 200, which will be tried first. The preparative chromatograph to be used for this purification study has been temporarily modified for higher sensitivity for the purpose. A mass spectrograph is also available for identification of impurities by mass analysis, but it is doubtful that its sensitivity will be better than a few ppm in the low molecular-weight range.

A sample handling system has been designed and is being constructed to facilitate transfer of the reactant samples from supply tanks to the chromatograph and the mass spectrometer. This system is shown schematically in Figure 2. It will be put into operation early in the second half of the first-year program.

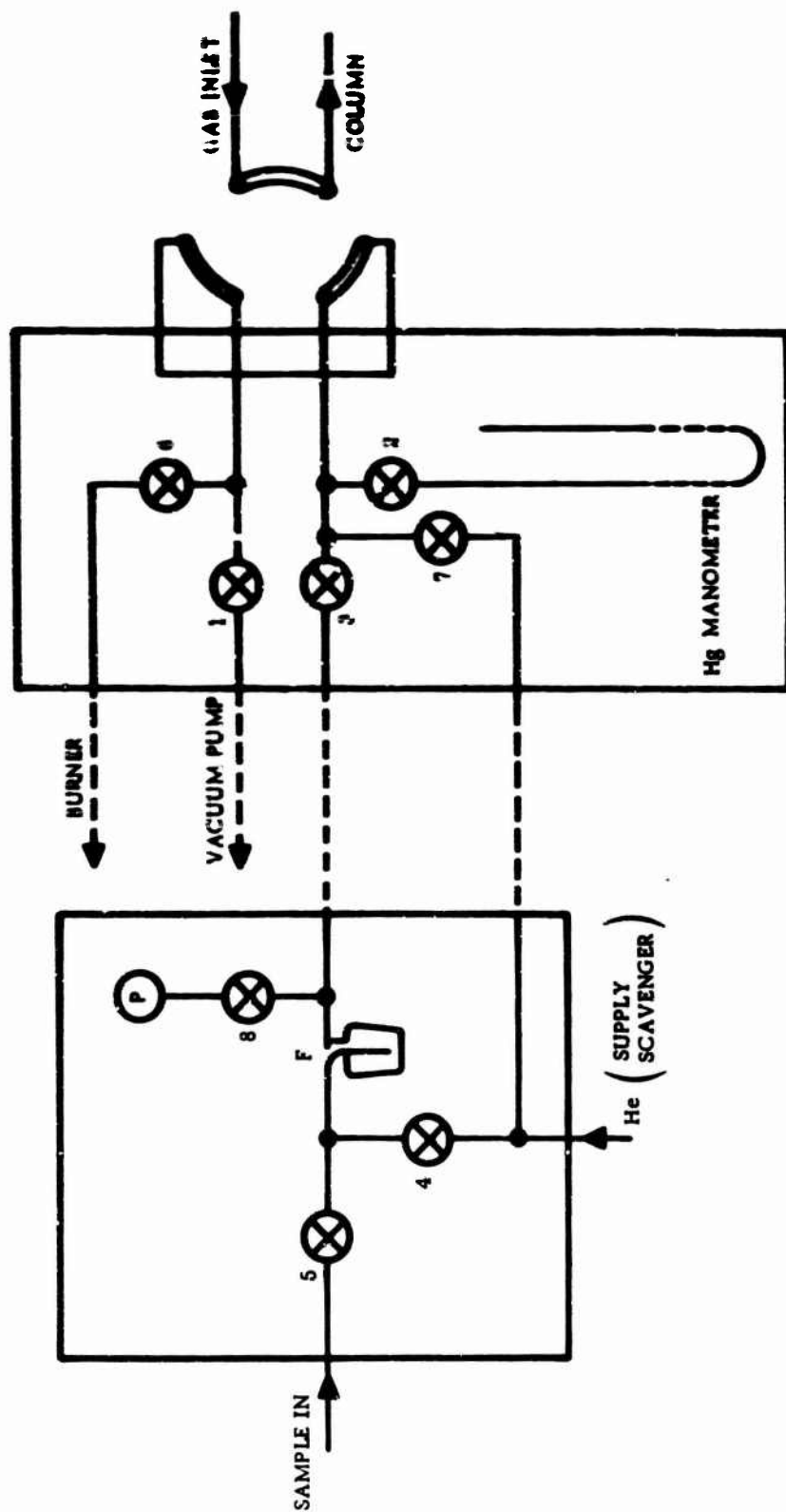
#### c. Subtask 5: Preparation and Characterization of Substrates

The routine preparation of polished wafers of both  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$  to provide substrates for the Si and GaAs deposition experiments has been under way from the beginning of the contract year. A major improvement has been made in the procedure for polishing  $\text{Al}_2\text{O}_3$  substrates for (111)Si growth, using synthetic diamond dust (1 $\mu\text{m}$  particle size) in the final polishing step. The surface finish now being obtained is the best yet achieved in the case of one  $\text{Al}_2\text{O}_3$  orientation which has been quite troublesome for polishing in the past. It has also been found that Linde "A" polishing compound (0.3  $\mu\text{m}$   $\alpha$ -alumina) can leave a residue on the  $\text{Al}_2\text{O}_3$  substrate surfaces which, unless removed by special techniques, survives routine predeposition cleaning procedures and prevents proper nucleation of CVD Si films.

A set of  $\text{Al}_2\text{O}_3$  substrate wafers has been selected for use in a series of analyses of the surface structure and impurity content in various stages of preparation for heteroepitaxial growth of semiconductor films. Techniques of Lang X-ray topography, scanning electron microscopy, low-energy electron diffraction, and Auger electron spectroscopy are to be utilized in these studies, in addition to conventional electron microscopy and electron diffraction analysis, X-ray diffraction analysis, and classical metallographic examination. These investigations were just beginning at the close of the six months period covered by this report.

#### d. Subtask 7: In Situ Studies of CVD Film Growth in the Electron Microscope

While the preliminary design of the necessary modifications in the AEI Model EM6 electron microscope to be used in these investigations was in progress it was decided that the in situ observations of CVD of semiconductors will be carried out at



F : Stainless steel flask (Vol ~ 500 ml)  
P : 0-100 psi manometer

NOTE: NUMBERED ITEMS ARE ON-OFF FLOW VALVES.

Figure 2. Schematic Diagram of Sample Handling System for Introducing Gas Samples Into Chromatograph and Mass Spectrometer

the Autonetics Research Center, requiring relocation of the instrument from the North American Rockwell Science Center. This has now been accomplished, with only a slight delay of the technical program resulting.

During the first six months of the program, a bibliography of previous research (primarily physical vapor deposition) related to the in situ chemical vapor deposition studies has been compiled. Contact has also been established with other researchers active in areas related to in situ film growth in the electron microscope.

Calculations based on the amount of scattering of 100 KeV electrons have shown that the resolution loss which will occur if the pressure of the gaseous reactants does not exceed 1 torr will be tolerable. These calculations are based on the assumption of a gas layer thickness of 1 mm in the direction of electron beam travel, which is the lower limit for a practical specimen holder design.

Various design alternatives have been considered for heating the specimen in these experiments, and a decision has been made to use an Agar-type (Ref 5) specimen heater (a resistively-heated stainless-steel mesh) rather than a furnace-type heater. The mesh-type heater has two significant advantages: (1) it is relatively easy to assemble and replace, and (2) it heats only the specimen, not the surrounding holder, thus reducing considerably the reaction of the reactant gases with the materials of the inlet tubes and the specimen holder.

Based on this heater configuration and the above thickness limitation, a specimen holder is being designed. The first specimen holder will permit translation of the specimen. As experience is gained in its use, a second holder will be designed which will also permit specimen rotation and tilting.

Various methods to provide auxiliary vacuum pumping in the specimen chamber area have been considered. It has been decided to modify the specimen chamber portion of the electron microscope column by installation of blank vacuum flanges containing apertures for the passage of the electron beam. This will permit differential pumping of the specimen chamber area with an auxiliary oil-diffusion pump. Although preferable from a cleanliness standpoint, an ion pump will not be used because of its extremely low throughput for the particular gases to be used. Design of the pumping system is under way, and the necessary pumps, valves, and fittings are being obtained. Preliminary design of the internal modifications in the electron microscope specimen chamber has also been initiated.

#### e. Subtask 8: Measurement and Evaluation of Film Properties

During the first six months of the program most of the investigations of Si heteroepitaxial growth on  $Al_2O_3$  and  $MgAl_2O_4$  substrates of various orientations involved nominally undoped Si. This was done since it was thought that the electrical properties of lightly doped films would be more sensitive to changes in various deposition parameters, as discussed earlier.

Results to date have indicated that in thin undoped Si films grown at temperatures <1050 C the apparent conductivity is n-type, with donor carrier concentrations varying from  $\sim 10^{12}$  to  $\sim 7 \times 10^{15} \text{ cm}^{-3}$  and some electron mobilities as high as  $700\text{--}850 \text{ cm}^2/\text{V}\cdot\text{sec}$ . These electrical characteristics are found, however, to be strongly influenced by surface conditions. For example, an as-grown Si/ $Al_2O_3$  film dipped in HF and rinsed in distilled deionized water may exhibit apparent electrical properties differing

by an order of magnitude or more from those of the same sample after an organic solvent rinse. It is apparent that observed electrical properties may be entirely dominated by surface-state conduction. For this to be the case, the estimated n-type surface charge density would be  $\sim 10^{11} - 10^{12} \text{ cm}^{-2}$ , which is not unreasonable for Si surfaces.

Due to the uncertainties appearing in the measurement of electrical properties of Si films with donor carrier concentrations less than  $\sim 10^{16} \text{ cm}^{-3}$ , the emphasis was shifted to the growth of As-doped Si, as indicated previously. Preliminary results have indicated that good quality n-type Si with both the (100) and (111) orientations can be grown on  $\text{Al}_2\text{O}_3$  at temperatures from 950-1050 C.

The electrical characteristics of a number of these samples are illustrated in Table I. These samples have been annealed for one hour in  $\text{O}_2$  at 1100 C, to simulate the conditions that might be encountered during device processing. In most cases, the as-grown characteristics are similar to those after annealing, although there is a tendency for the electron mobilities to increase slightly after anneal. In general, the (111) and (100) Si growths appear to have nearly equivalent electrical properties. It should be pointed out, however, that the effects of surface conduction on the electrical characteristics of these samples have not yet been determined. Until such studies are completed the results given in the table are to be considered as provisional.

The growth of nominally undoped Si above a temperature of 1050 C in either  $\text{H}_2$  or He atmosphere typically yields p-type films, the acceptor commonly being identified as Al transferred from the substrate during growth. A few films not intentionally doped have been grown at temperatures from 1100 to 1200 C. The electrical properties of the best of these films are shown in Table II. However, the characteristics of these films are also considered provisional until the effects of surface conduction have been established.

During the period covered by this report, routine electrical measurements were also carried out at UCLA, with a twofold objective -- to provide a verification of the accuracy of measurements made at Autonetics and to establish measuring techniques at UCLA identical to those employed at Autonetics, for use later in the program

In addition to routine measurement of resistivity, carrier concentration, and mobility by the Hall effect, infrared reflectivity and transmissivity measurements were made in the wavelength region from 3 to 40 microns. The infrared measurements are useful for determination of the thickness of the semiconductor film and determination of the optical constants of the film material. The thickness is obtained from the interference pattern in the infrared reflectance spectrum. The optical constants will be determined with the assistance of a computer program written for use with reflectivity and transmissivity data.

Table I  
Electrical Properties of Arsenic-Doped Si/Al<sub>2</sub>O<sub>3</sub>

Growth Temp. (C)	Thickness (μm)	Carrier Gas	Si Film Orientation	Resistivity (ohm-cm)	Carrier Concentration (cm <sup>-3</sup> )	Carrier Mobility (cm <sup>2</sup> /V-sec)
950	1.7	He	(100)	0.24	5.9 x 10 <sup>16</sup>	450
	1.7	He	(111)	0.26	7.3 x 10 <sup>16</sup>	330
	1.9	He	(100)	0.12	1.3 x 10 <sup>17</sup>	400
	1.9	He	(111)	0.15	1.3 x 10 <sup>17</sup>	330
	1.9	He	(100)	0.080	2.3 x 10 <sup>17</sup>	350
	1.2	He	(111)	0.060	2.1 x 10 <sup>17</sup>	500
	1.5	He	(100)	0.097	2.1 x 10 <sup>17</sup>	320
1000	1.8	He	(100)	0.15	1.0 x 10 <sup>17</sup>	410
	2.0	H <sub>2</sub>	(111)	0.12	8.7 x 10 <sup>16</sup>	580
	2.2	H <sub>2</sub>	(100)	0.11	1.1 x 10 <sup>17</sup>	530
1045	2.7	H <sub>2</sub>	(111)	0.17	6.7 x 10 <sup>16</sup>	560
	2.7	H <sub>2</sub>	(100)	0.14	9.8 x 10 <sup>16</sup>	460

**Table II**  
**Electrical Properties of As-Deposited P-Type (111) Si**  
**on Several Orientations of  $A_2O_3$**

<b>Growth Temp. (C)</b>	<b>Thickness (<math>\mu m</math>)</b>	<b>Carrier Gas</b>	<b>Resistivity (ohm-cm)</b>	<b>Carrier Concentration (<math>cm^{-3}</math>)</b>	<b>Carrier Mobility (<math>cm^2/V\text{-sec}</math>)</b>
1095	9.0	H <sub>2</sub>	0.90	$2.3 \times 10^{16}$	310
1100	1.3	He	0.84	$2.2 \times 10^{16}$	340
	5.6	He	2.3	$7.1 \times 10^{15}$	380
1150	2.3	H <sub>2</sub>	0.20	$1.5 \times 10^{17}$	210
	10.5	H <sub>2</sub>	0.20	$1.2 \times 10^{17}$	270
	10.9	H <sub>2</sub>	0.28	$1.1 \times 10^{17}$	220
	5.1	He	1.8	$1.1 \times 10^{16}$	310
	5.7	He	0.68	$2.2 \times 10^{16}$	420
	6.7	He	0.76	$2.5 \times 10^{16}$	330
	6.9	He	0.62	$2.5 \times 10^{16}$	410
1200	10.0	H <sub>2</sub>	0.17	$1.2 \times 10^{17}$	300
	10.1	H <sub>2</sub>	0.20	$1.4 \times 10^{17}$	220
	4.3	He	0.20	$1.4 \times 10^{17}$	220

A microwave method of measuring carrier concentration without attaching electrodes to the samples has been tested on bulk samples, and it is now being extended to the heteroepitaxial films. This technique has the further advantage that it can be very easily extended to lifetime measurements. The method depends upon the absorption of microwave power in a semiconductor window through which a microwave beam is propagated.

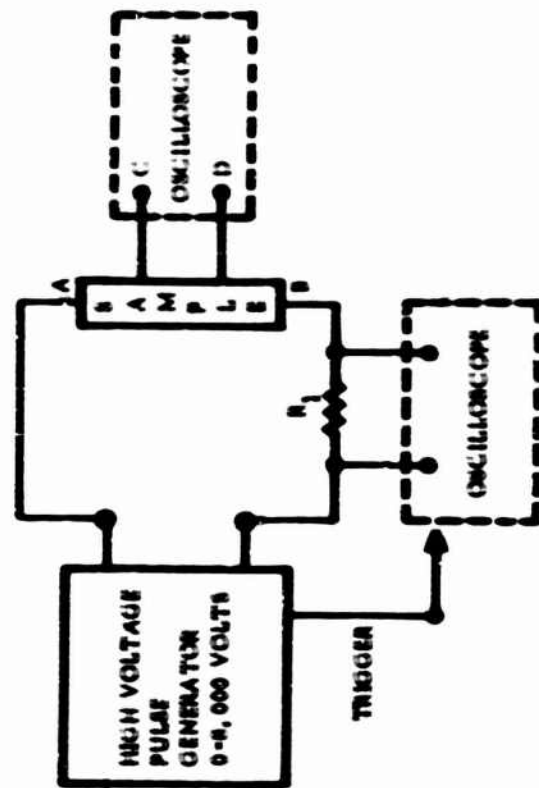
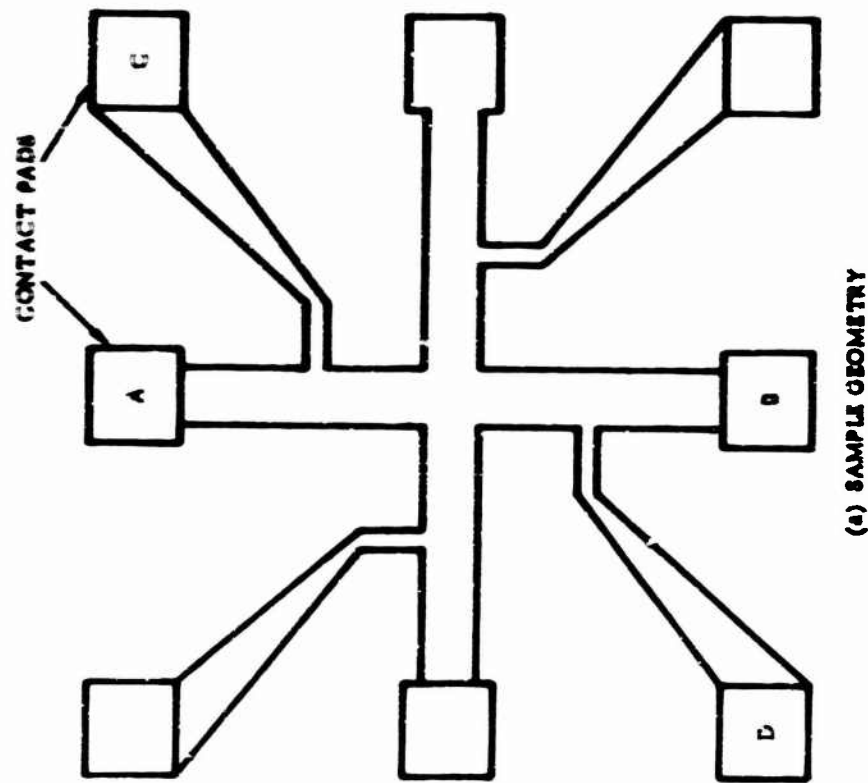
A conventional high-voltage pulse technique has been used to study the current density-versus-electric field ( $J$  - vs.  $-E$ ) characteristics of GaAs-on- $Al_2O_3$  heteroepitaxial films. A d-c pulse of approximately 10- $\mu$ sec width and 1 percent duty cycle was applied across ohmic contacts at either end of a long "bar" sample of heteroepitaxial GaAs. Figure 3a shows the Hall-effect bridge-sample pattern adapted for these  $J$  - vs.  $-E$  measurements. By measuring on an oscilloscope the voltage developed at two intermediate ohmic contact points at known locations along the bar and simultaneously monitoring the voltage developed across a known resistance in series with the sample (see Figure 3b) the  $J$ - $E$  characteristic was determined. Using this technique, good agreement was obtained with the low-field mobility data obtained with the Hall effect. However, to determine the carrier mobility, or more precisely, the carrier velocity-versus-electric field ( $v$  -  $E$ ) characteristics from such data is difficult. A precise evaluation of the  $J$  -  $E$  characteristic requires a detailed Boltzmann-equation analysis of high-field carrier transport, with consideration of the various mechanisms responsible for energy relaxation and intervalley carrier transfer. In heteroepitaxial GaAs, with unknown concentrations of vacancies and other defects present, this technique at best will yield an indirect and uncertain value for carrier mobility.

It became apparent that a direct method of measuring the velocity-field characteristic was needed. In such a method it would be only necessary to measure the velocity of carriers over a wide range of electric field values rather than to measure the  $nv$  product (current density). Such a method has been developed and is discussed in the following section.

#### f. Subtask 9: Design and Fabrication of Devices in Improved Films

Although this work is not planned for full activation until later in the program, some preliminary work on simple device structures has been initiated at UCLA. In connection with this preliminary work, a novel method of measuring high-field transport properties has been developed. This method, which uses a time-of-flight measurement technique, appears suitable for both bulk and thin-film samples.

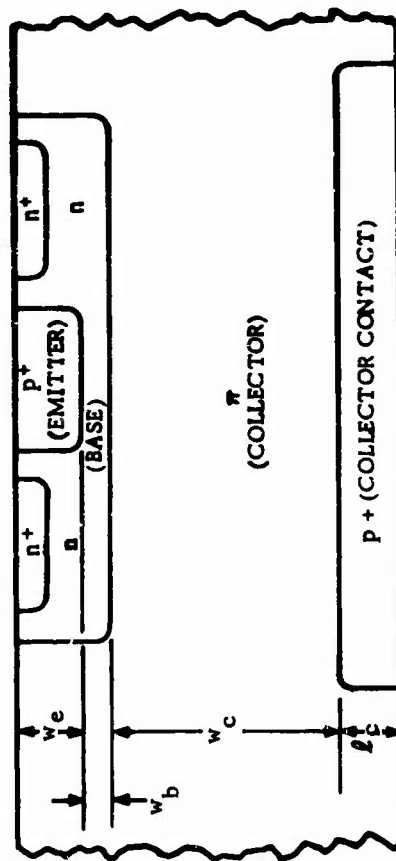
The technique employs a transistor structure (Figure 4a) in which the emitter-base junction is used to inject a pulse of excess carriers into the depletion region of a high-resistivity collector. The collector is held in a "swept-out" condition, that is, with the depletion layer extending throughout the collector region to the high-conductivity  $p^+$  contact. Assuming a uniform electric field exists over the relatively long depletion layer, the carriers will travel at essentially constant velocity through this region. This in turn induces a constant current in the external collector circuit, which remains for as long as the carriers are in transit through the collector. By monitoring both the base and collector currents it is possible to obtain, with a knowledge of the width of the collector region, a direct measurement of carrier velocity for a known electric field. The electric field may be varied simply by changing the collector-base bias voltage ensuring, of course, that the fully "swept-out" condition remains.



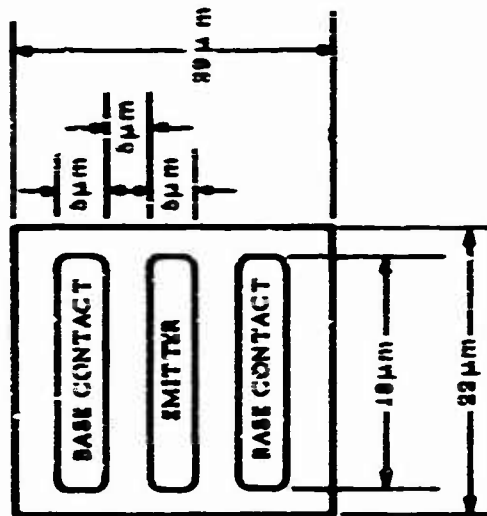
(b) PULSE MEASURING CIRCUIT

Figure 3. Sample Geometry and Circuit for Pulse-type Measurement of J-E Characteristic of Semiconductor Films





(a) CROSS SECTION VIEW OF  
P<sup>+</sup> - n - π - p TRANSISTOR



(b) DIMENSIONS OF COLLECTOR JUNCTION,  
EMITTER AND BASE CONTACT

Figure 4. P<sup>+</sup> - n - π - p<sup>+</sup> Transistor Geometry for Measurement of High-field Transport Properties

An over-riding limitation in any time-of-flight measurement of excess carriers is set by the dielectric relaxation time  $\tau_D$ , where,

$$\tau_D = \epsilon \rho. \quad (21)$$

with  $\epsilon$  the dielectric constant and  $\rho$  the resistivity of the material. For Si and for  $\tau_D \geq 10^{-8}$  sec it follows that  $\rho \geq 10^4$  ohm-cm. The value of  $\tau_D$  sets an upper limit on the transit time of the carriers that can readily be measured and also demands that high resistivity material be employed.

The saturation velocity of holes in Si is  $v_h(\text{sat}) = 8 \times 10^6$  cm/sec. If  $t_c$  = transit time of carriers across the depletion region of length  $L_c$ , then for  $t_c \approx 10^{-8}$  sec the maximum length becomes

$$L_{\text{max}} = v_h(\text{sat}) \times t_c \approx 8 \times 10^{-2} \text{ cm} = 800 \mu\text{m} \quad (22)$$

The total delay time in the response of the collector current when a voltage pulse is applied to the emitter-base junction is  $\tau_{ec}$ , where

$$\tau_{ec} = \tau_e + \tau_b + \tau_c + \tau_{si}. \quad (23)$$

and  $\tau_e$  is the emitter-barrier charging time,  $\tau_b$  is the base transit time,  $\tau_c$  is the collector depletion-layer charging time, and  $\tau_s$  is the transit time of carriers across the collector depletion layer.

$\tau_e$  is an RC product of the emitter series resistance  $r_e$ , given by  $kT/eI_E$ , and  $C_e$ , the emitter barrier capacitance. If the emitter junction potential is defined as  $V_e = \phi - V_o$ , with  $\phi$  the junction barrier potential,  $V_o$  the applied voltage,  $A_e$  the area of the emitter-base junction,  $g$  the junction grading factor, and  $a$  being a parameter between 3 and 8 which accounts for the doping profile of the emitter departing from an ideal graded junction, then

$$C_e = A_e \left( \frac{\epsilon^2 e g}{a V_e} \right)^{1/3} \quad (24)$$

$$\text{and } \tau_e = \frac{kT}{e} \frac{A_e}{I_E} \left( \frac{\epsilon^2 e g}{a V_e} \right)^{1/3}. \quad (25)$$

For the geometry shown in Figure 4a and 4b  $\tau_e \approx 0.01 \times 10^{-9}$  sec.

The time constant associated with the mobility of minority carriers in the base region is

$$\tau_b = \frac{w_b^2}{nD}, \quad (26)$$

where  $w_b$  is the base thickness,  $D$  the minority carrier diffusion coefficient, and  $n$  a factor related to the drift field in the base region associated with the impurity gradient. The parameter  $n$  has a value of 4 for diffused-base and step-junction emitter structures. For the model transistor,  $\tau_b = 0.015 \times 10^{-9}$  sec.

$\tau_c$  is the collector depletion-layer charging time and is determined by the RC product  $r_c' C_1$ , where  $r_c'$  is the resistance in series with the inner collector depletion-layer capacitance  $C_1$ . Neglecting spreading resistance,  $\tau_c$  is given by

$$\tau_c = \rho_c l_c \left[ \frac{e \epsilon N_c}{2 V_c} \right]^{1/2} \quad (27)$$

where  $\rho_c$  is the  $p^+$  collector layer resistivity,  $l_c$  the length of the  $p^+$  region in series with the depletion region,  $N_c$  the doping concentration in the collector depletion region, and  $V_c$  the collector voltage. For the present design  $\tau_c = 1 \times 10^{-12}$  sec.

The transit time  $\tau_s$  of carriers traversing the collector depletion region is simply  $\tau_s = w_c/v_s$ , where  $w_c$  is the depletion layer width and  $v_s$  is the drift velocity of the carriers. For the model transistor the transit time is  $\approx 10 \times 10^{-9}$  sec.

From these calculations it is seen that the present emitter-base structure is capable of providing at the base-collector junction a pulse of holes having a rise (or fall) time of less than  $0.05 \times 10^{-9}$  sec. A Hewlett-Packard HP125A pulse generator applied across the emitter-base junction is capable of providing a voltage pulse from 0 to 10 volts with a pulse width of from 1 to  $100 \times 10^{-9}$  sec and a rise (or fall) time of approximately  $0.3 \times 10^{-9}$  sec.

To obtain accurate measurement of the pulse width on a sampling oscilloscope, it is desirable to have collector-current pulse widths of two or more nanosec. This requires a depletion layer width of

$$w_c \geq v_h (\text{sat}) \times T \quad (28)$$

or

$$w_c \geq 160 \mu\text{m} \quad (29)$$

The present design of the transistor structure has depletion layer widths from 200 to  $800 \mu\text{m}$ , easily satisfying this condition.

Initial experiments with this new method have been performed on high resistivity bulk Si wafers. The method will be adapted for the study of high-field transport properties of heteroepitaxial films in the next six-month period. At this point, a basic design has been completed and masks have been made. Experiments will be performed on the heteroepitaxial devices made by this design, and the results will be used to optimize the design.

### SECTION III

#### WORK PLANNED FOR SECOND SIX MONTHS

The work planned for the second six months of the contract constitutes mainly extensions of work already in progress. In addition, Subtasks 6 and 9 (see Section II) will become fully active, so that the entire program will be underway along the general lines described in the initial technical proposal. The plans for the balance of the first contract year are outlined briefly, by subtask, in this section.

##### 1. THEORETICAL STUDIES

The regular interactions between theoreticians and experimentalists will increase, both in frequency and in depth of involvement of the theoreticians in day-to-day experimental problems. It is expected that the experimental characterization of real surfaces will be well under way and that means of improving and perfecting them will be under investigation, so that theory can be more adequately used in delineating mechanisms.

Additional effort will be devoted to development of the two theoretical investigations already in progress, as follows.

##### a. Subtask 1: Classical Epitaxy Theory - Nucleation, Kinetics, Crystallographic Relationships

During the second six months the "gaussian replacement method" will be applied to real films on "perfect" surfaces of real substrates, probably Si on both  $Al_2O_3$  and spinel. Attempts will be made to employ not only realistic geometries but also somewhat realistic potentials derived by one or more empirical means (for example, by analysis of Morse potentials). Attempts will then be made to apply the method to substrate surfaces containing simple defects in order to see how far this theoretical approach can be carried in the discussion of real systems.

##### b. Subtask 2: Theoretical Studies of the Quantum Mechanics of Surfaces

In the second six months of the program, the phenomenological pairwise interatomic potential calculation of interfacial binding energy between Si and  $Al_2O_3$  will be performed for orientations of interest in the experimental program. Elastic deformation near the interface will be permitted, and the elastic energy will be included in the total energy. By employing the same phenomenological potentials and methods of calculation, the position/orientation-dependent features of the various crystal growths can (in principle) be determined. Of special interest will be any orientations which produce large amounts of elastic strain and stress. It is expected that these studies will be completed during the second six months. A second investigation which may be started, but not completed, by the end of the year is the pseudopotential calculation of interfacial and surface electronic energy bands.

## 2. EXPERIMENTAL STUDIES

Several of the experimental subtasks have only recently become fully activated. As a result, the second six months will witness an acceleration of the experimental program and an increase in the interplay among the various experimental activities. The anticipated work in this part of the contract program for the remainder of the year is as follows.

### a. Subtask 3: CVD Delivery Kinetics and Film Preparation

During the second six months of the contract year the Si growth studies will be continued, using  $\text{AsH}_3$  as the source of n-type dopant. Growth comparisons will continue to be made for the Si-on- $\text{Al}_2\text{O}_3$  and Si-on-spinel systems. During this study, attempts will be made to correlate growth parameters with the properties of the substrate as they are related to substrate orientation. Particular attention will also be given to examining the effect of substrate surface etching on film quality.

Deposition parameter studies, examination of the kinetics of the chemical reactions involved, and preparation of films for experimentation in the GaAs-on- $\text{Al}_2\text{O}_3$  and GaAs-on- $\text{MgAl}_2\text{O}_4$  systems will also be initiated in the second half of the first year. It is likely that major emphasis will continue to be placed on Si film growth in this period, however.

### b. Subtask 4: Analysis and Purification of CVD Reactants

During the second half of the first year, the apparatus for handling and transferring samples of air-sensitive materials will be completed and tested. Methods of analysis for trace contaminants in  $\text{SiH}_4$ ,  $\text{AsH}_3$ , and trimethylgallium (TMG) will be designed, tested and used to check starting materials as available. Major impurities will be detected initially by mass spectrometry. Because of the limited sensitivity of this instrument (AEI Spectrometer Model MS-9), impurities in the parts per billion range will not be observed. For ultratrace contaminants, presently available gas chromatographs will be modified and rebuilt as necessary. Unknown compounds may be identified by retention characteristics or by enrichment followed by mass spectrometry. Concurrently, efforts to purify starting reactant materials by preparative gas chromatography will be initiated.

### c. Subtask 5: Preparation and Characterization of Substrates

The activities of this subtask in the second six months will include both continued routine preparation of a variety of substrates for Si and GaAs deposition experiments and also detailed analyses of the surface structure and impurity content of substrates at various stages of preparation for use in heteroepitaxial growth experiments. These analyses will be carried out on the set of  $\text{Al}_2\text{O}_3$  substrate wafers already selected for the purpose and also on a similar set of  $\text{MgAl}_2\text{O}_4$  substrates, in the same manner. Many of these thoroughly characterized substrates will be subsequently used for both Si and GaAs heteroepitaxy, to permit correlation of substrate properties with the results of the deposition experiments and the properties of the deposited films. In some cases experimental device structures will be fabricated in these films to extend

further the correlative considerations. These studies are considered to be an extremely important part of the program, since it is quite clear that the initial stages of nucleation and growth of a heteroepitaxial film are strongly dependent on the details of the physical and chemical condition of the substrate surface. Increasingly stringent and controlled substrate preparation and cleaning procedures will be developed and utilized as the program progresses.

d. Subtask 6: Correlation of Film Properties with Substrate Properties and CVD Process Parameters

The activities appropriate to this subtask are interwoven among all of the other subtasks of the program. Correlation of various aspects of the experimental results will be a continuing process, and correlation of experimental results with some of the theoretical analyses will be undertaken when appropriate.

e. Subtask 7: In Situ Studies of CVD Film Growth in the Electron Microscope

It is anticipated that the second six months of the program will involve the following activities in this subtask:

1. The photographic set-up for motion-picture recording of in situ film growth will be completed and tested.
2. Hot-stage experiments will be performed whereby single-crystal thin films of Zn, Cu, or Si will be oxidized in the existing microscope vacuum.
3. Fabrication of the necessary parts will be completed and a physical vapor deposition experiment will be conducted in the existing microscope vacuum. Au, Zn, or Cu will be deposited onto amorphous carbon or single-crystal Si in this experiment.
4. The design, fabrication and installation of the auxiliary vacuum pumping system will be completed.
5. The design of the specimen chamber modifications required for differential pumping will be completed and fabrication begun.
6. The design of the "pressurized" (1 torr) specimen holder with heating element will be completed and fabrication begun.
7. A technique will be developed for thinning single-crystal-Si for making electron-transparent substrates.

f. Subtask 8: Measurement and Evaluation of Film Properties

The electrical evaluation measurements to be carried out in the second six months will constitute primarily a continuation of the studies already in progress. Due to the uncertainty inherent in the electrical characteristics of undoped n-type

Si films, emphasis will be shifted to evaluation of doped Si films grown with carrier concentrations greater than  $10^{16}\text{cm}^{-3}$ . At these concentrations the relative contribution of surface states to the electrical conductivity can be reduced so that the bulk properties of the material can be more accurately ascertained. By the end of the first year of the program it is anticipated that optimum growth conditions for Si epitaxy by CVD may have been determined, as well as the Si orientation and substrate composition and orientation which lead to the best Si film properties. However, the study of surface-state conduction in undoped Si films will be continued in order to determine the factors which most strongly influence the surface conductivity. In addition, measurement techniques which might distinguish between surface and bulk conduction will be investigated during the second six months so that the true bulk conductivity and related parameters can be deduced for high-resistivity films.

It is expected that some measurements on heteroepitaxial films in the GaAs-on-insulator system will also commence during the second six months as deposition and reaction kinetics studies with GaAs are initiated. Routine structural evaluation of the heteroepitaxial films by means of classical metallographic methods, X-ray diffraction procedures, and reflection electron diffraction techniques will also continue.

In addition, it is expected that microstructure investigations will be undertaken by special X-ray diffraction and related techniques. The microstructure of an epitaxial layer is influenced by the details of the initiation, growth, and coalescence of the nuclei and the post-nucleation islands. Detailed investigation of film microstructure is expected, therefore, to yield information from which can be inferred certain aspects of the mechanisms of the early stages of film formation. The microstructure also represents the status of defect type and concentration, which defects have important implications for the electrical behavior of the film. These microstructure studies will be closely coordinated with the theoretical studies of film nucleation and growth, substrate characterization, deposition parameter investigations, and electrical characterization of the films. It is anticipated that the microstructure studies will make use of specialized X-ray diffraction techniques including Lang topography, double-crystal spectrometry, recently-developed Kossel-line topography, and other appropriate techniques.

An interesting new technique which, on the basis of some preliminary experiments with heteroepitaxial films of GaAs on  $\text{Al}_2\text{O}_3$ , appears to offer promise of major success for evaluating the structural perfection (and related properties) of the important interfacial region in a heteroepitaxial system is the observation of the energy spectrum of the back-scattered protons from a proton beam injected into the crystalline film in appropriate crystallographic directions. This recently developed technique, useful for determining whether implanted impurity ions are located on interstitial or substitutional lattice sites in a host crystal, is very sensitive to lattice disorder and permits locating regions of disorder at various depths into a crystal. During the second six months of the program the possibilities of evaluating film perfection and obtaining defect density distributions as a function of depth in the interfacial region of heteroepitaxial films of Si and of GaAs will be investigated experimentally. Proton beam energies up to 0.5 MeV from a Van de Graaff accelerator, together with all of the necessary auxiliary equipment and techniques for making detailed channeling and back-scattering measurements, are available at the North American Rockwell Science Center and will be used in these studies.

**g. Subtask 9: Design and Fabrication of Devices in Improved Films**

The new method for measuring the high-field transport properties of semiconductors, which has been developed with bulk crystal semiconductors in the first part of the program, will be adapted for the study of these properties in epitaxial films in the second half of the year. This will involve the design of a suitable transistor geometry for heteroepitaxial films and the fabrication of devices in these films. In addition, p-n junctions will be fabricated to study the exponential dependence of the I-V characteristics to identify the source of the current and to analyze the reverse current. Other related junction and device measurements will be made to determine the doping profile and other characteristics, to assist in evaluating the feasibility of using these films in various device applications. These device-based measurements will be made in films of both Si and GaAs, on substrates of  $Al_2O_3$ ,  $MgAl_2O_4$ , and possibly BeO.



## SECTION IV

### PROGRAM SUMMARY FOR FIRST SIX MONTHS

The overall objective of this program, for which this is the first Semi-annual Technical Report, is to carry out a fundamental study of the nucleation and film growth mechanisms in heteroepitaxial semiconductor thin films, leading to new knowledge and understanding of these processes, and then to apply these results to the preparation of improved semiconductor thin films and thin-film devices on insulating substrates.

The specific technical objectives of the three-year program are the following:

1. Investigation of the many aspects of the mechanisms of heteroepitaxial film growth, to establish (through accumulation of basic knowledge) sets of technical guidelines for the preparation of better films which can then be applied to real situations.
2. Preparation of improved, high-quality, device-grade heteroepitaxial films of Si and GaAs on insulating substrates by chemical vapor deposition (CVD) methods.
3. Development of methods of characterizing heteroepitaxial films as to their suitability for subsequent device fabrication.
4. Design and fabrication of selected thin-film devices which take advantage of the unique properties of such films.

The program involves both theoretical and experimental investigations of heteroepitaxial films in semiconductor-insulator systems. The theoretical studies in the program are of two types. First, there is direct response to the needs of the experimental program involving data analyses, theories and explanations, and guidance in identifying definitive experiments. Second, original exploration of theoretical topics of fundamental importance to the field of epitaxy will continue throughout the program; the goal of such theoretical studies will be the generation of significant theoretical advances in the field of heteroepitaxy.

The experimental investigations are also of two types. First, fundamental explorations are undertaken to elucidate mechanisms and general principles of the heteroepitaxial growth process. Second, practical studies accompany the fundamental investigations so that useful discoveries and developments can be immediately applied to improve the properties of the semiconductor films, which can then be utilized in fabricating experimental devices.

CVD methods are the most common and successful in use for film growth in the semiconductor industry. The emphasis in this program is on such techniques. Most previous fundamental studies of epitaxy have concentrated upon physical vapor deposition (PVD) methods, partly because both experimental and theoretical scrutiny are easier with these techniques. However, they will be employed in this program only at those times when they are helpful in the search for understanding with CVD methods.

Si and GaAs are to be used for most of the work, together with substrates of sapphire ( $Al_2O_3$ ), spinel (both stoichiometric and nonstoichiometric), and beryllia ( $BeO$ ). Si and GaAs have been chosen because of the preeminence of the former in the semiconductor industry and the high-frequency and high-temperature attributes of the latter; in addition, they represent the elemental and compound semiconductors for which most comparative information exists.

Si-on  $Al_2O_3$  and GaAs-on- $Al_2O_3$  are the semiconductor-insulator systems to be emphasized, based in part on the success already achieved with these systems and in part on their potential value to device technology. However, if it becomes advisable as the program develops, other semiconductor-insulator combinations are to be brought into consideration.

The research has been divided into nine subtasks, as follows:

#### Theoretical Studies

Subtask 1: Theoretical examination of CVD kinetics and the processes of nucleation, surface migration, and film growth with emphasis on crystallographic relationships between overgrowth and substrate, using both "classical" and recently developed techniques and concepts, to attempt to identify mechanisms and establish general principles of heteroepitaxial growth.

Subtask 2: Calculation of interfacial (surface) binding energies and other parameters involving the quantum mechanics of surfaces and interfaces, based primarily on the pseudopotential approach.

#### Experimental Studies

Subtask 3: Investigation of the delivery kinetics of CVD processes, to improve the detailed understanding and control of the chemical reactions involved in the preparation of heteroepitaxial semiconductor films by CVD; also, preparation of films for use in other parts of the program.

Subtask 4: Analysis and purification of reactant materials used in metal-organic-hydride and other CVD processes; preparation of sample quantities of improved-purity reactants so that films of higher quality can be obtained.

Subtask 5: Preparation of substrates and characterization of surfaces and impurity content of substrates for use in semiconductor heteroepitaxy, with particular attention to such factors as surface orientation, defect structures, and surface purity.

Subtask 6: Correlation of properties of grown heteroepitaxial semiconductor films with measured substrate properties and CVD process parameters, and explicit experimental verification of these correlations.

Subtask 7: In situ observation and study of the early stages of growth of CVD films in the electron microscope, to develop additional fundamental knowledge of the epitaxy process. Results of these experimental observations will be incorporated into the theoretical studies wherever possible.

Subtask 8: Measurement of the electrical, optical, crystallographic, and thermal properties of heteroepitaxial semiconductor films on insulators, by a variety of measurement techniques. Standard techniques will be employed and new methods developed where required, for measurement of those film properties which best characterize ultimate device performance.

Subtask 9: Design and fabrication of certain types of devices using some of the heteroepitaxial films produced in the above studies, both to evaluate material properties and to exploit semiconductor film characteristics unique to heteroepitaxial systems.

The accomplishments of the first six months are summarized as follows:

## 1. THEORETICAL STUDIES

The method of replacing the atoms of an overgrowth on a substrate with gaussian mass distributions, which interact with the substrate as a function of position in the same way as real atoms, has permitted the development of these "atoms" into an overgrowth the effective density of which is represented as a rapidly converging expansion in the reciprocal lattice. This makes it possible to study the orientational and misfit potential between film and substrate.

The method has been extensively developed and applied in detail to the determination of crystallographic relationships between square lattice overgrowths and substrates. It is possible to compute the interaction energy between film and substrate for any lattice parameters and any mutual orientation of film and substrate. In order to determine the preferred orientation, rotations are carried out until the film comes (in some orientation) into near commensurability with the substrate. Then pseudomorphic deformation is assumed to occur, leading to precise commensurability. The elastic strain energy corresponding to this pseudomorphic deformation is then added to the interface energy, and the sums corresponding to different orientations at which pseudomorphic registry is possible are then compared. Those sums which lead to the lowest total energy represent preferred orientations.

The method is applicable to films of infinite extent and to islands of finite size and irregular shape, and has been applied to both of these cases for this simple case of heteroepitaxy. As a result, all of the crystallographic relationships for this case have been generated. Refinements in the method are now being developed. (See Section II-1-a.)

In a second theoretical investigation, the principal activity has been the investigation of theories and theoretical approaches to the problems of cohesion and structure as applied to heteroepitaxy. The three theoretical problems of a direct-effect nature — i. e., those involving film — substrate crystallographic relationships for "substantially ideal" films and "substantially ideal" substrates — believed to be most relevant to the experimental heteroepitaxy investigations are: (1) the interfacial cohesive and binding energy between film and substrate, (2) the interfacial-state energy bands and associated electronic conductivity, and (3) the film surface-state energy bands and associated electronic conductivity. The first of these three problems has received the most attention to date.

In these theoretical studies, an attempt has been made to develop a method of calculation of interfacial binding energy between film and substrate which is more realistic (and therefore useful) than previous calculations of a similar nature. To whatever extent possible, the binding-energy calculational model should be based on solid-state quantum mechanics. The original intent was to perform a Green's function/Wannier-basis calculation of the one-electron redistribution energy of the interface. (This redistribution energy is the effective binding energy.) Further investigation of this approach, which would be an explicitly quantum-mechanical treatment utilizing first principles, led to the conclusion that such a procedure is not feasible within the time scale and available level of effort of the total contract program.

Consequently, a different approach is being used for calculation of interfacial binding energies. The model presently being developed is a semi-phenomenological treatment which employs a relatively short-range pairwise interatomic interaction potential between Si atoms and the Al-O atoms lying in and near the interface. Provided the interatomic potentials can be determined and are found to be of relatively short range, the binding energy can be calculated with computers. The relative orientations of the interfacial film-substrate planes can then be varied, and in this way the orientation dependence of the binding energy can be determined. The actual total energy will, however, include elastic contributions due to the relaxation from the "ideal" bulk configuration into an atomic configuration with greater (negative) binding energy at the expense of elastic (positive) energy. In the interest of practicality, a pseudomorphic distortion or strain will be employed which is maximum near the interface and dies off toward the free surface of the film according to classical elasticity theory. The studies are proceeding along these lines. (See Section II-1-b.)

## 2. EXPERIMENTAL STUDIES

The emphasis in the experimental studies in the first six months has been on the preparation of heteroepitaxial films of Si on substrates of  $Al_2O_3$  and  $Mg Al_2O_4$  by a CVD process involving the pyrolysis of silane under a variety of experimental conditions, on the evaluation of the results of these parameter studies in terms of the structural and electrical properties of the films, and on the modification of an electron microscope for use in the *in situ* observation of the growth of CVD semiconductor films on insulating substrates.

In the first year of the program it is intended that both the Si-on-insulator and the GaAs-on-insulator systems be investigated, with attention directed toward identifying the following in both systems: (1) preferred substrate; (2) optimum growth temperature; (3) preferred film orientation; (4) preferred growth atmosphere; (5) preferred substrate orientation; and (6) optimized over-all growth process.

During the first six months of the program, studies of the effects of various growth parameters and other variables on the quality of Si films grown on  $Al_2O_3$  and  $Mg Al_2O_4$  substrates were undertaken. Particular attention was paid to growth on  $Al_2O_3$ , although considerable interest has been generated in  $Mg Al_2O_4$  as a possible preferred substrate for Si growth, based primarily on a comparison of the electrical properties of (100) Si growth on (01 $\bar{1}$ 2)  $Al_2O_3$  with those of (111) Si growth on (111)  $Mg Al_2O_4$ . It is important to note, however, that high quality (111) Si growth has also been reported on (0001)  $Al_2O_3$ ; there are several orientations of  $Al_2O_3$  that promote (111) Si growth. Since one of the objectives of the program is the preparation of high-quality Si films on insulating substrates, comparative Si growth data on  $Al_2O_3$  and

Mg  $Al_2O_4$  have been accumulated and evaluated. These studies will permit a realistic determination of the preferred substrate for heteroepitaxial Si, based on criteria of growth temperature, film orientation, growth atmosphere, and substrate surface quality and orientation.

Nominally undoped Si films were used in the initial work in the expectation that the electrical properties of such films would be more sensitive to changes in CVD growth parameters, substrate conditions, and other controllable factors. However, it was determined that the properties of thin undoped Si films grown at temperatures less than 1050 C are dominated by surface conduction. Such films are n-type, with donor carrier concentrations varying from  $\sim 10^{12}$  to  $\sim 7 \times 10^{15} \text{ cm}^{-3}$  and some electron mobilities as high as 700 to 850  $\text{cm}^2/\text{V-sec}$ , but the characteristics vary greatly with surface treatment.

It thus appeared expedient to add an n-type dopant, in this case As, to the growing films and establish conditions for growth with donor carrier concentrations from  $10^{16}$  to  $> 10^{18} \text{ cm}^{-3}$ , where the effects of the Si surface might be minimized. The electrical results obtained on such films to date verify the achievement of good quality n-type (111) and (100) Si growth on  $Al_2O_3$  at growth temperatures as low as 950 C.

The experiments have also indicated that at temperatures  $> 1050$  C nominally "undoped" Si films grown in  $H_2$  or He are invariably p-type (due to autodoping), but n-type when grown at 1000 C. The preferred growth temperature range for Si heteroepitaxy on  $Al_2O_3$  is thus found to be  $\sim 950 - 1050$  C to provide nearly equivalent high-quality (100)- and (111)-oriented films essentially uncompensated by Al. However, the role of surface conduction in the properties of these films is not yet fully evaluated. (The above temperature range is also found to be usable for Si growth on (111)-oriented Czochralski-grown Mg  $Al_2O_4$ .)

The results of some recent preliminary Si growth experiments on crystallographic orientations of  $Al_2O_3$  that have thermal expansion coefficients lower than that of Mg  $Al_2O_4$  and closer to that of Si have been encouraging. The investigations are being continued. (See Section II-2-a.)

The routine structural evaluation of the films has been achieved by X-ray and electron diffraction and standard metallographic techniques. Routine electrical measurements of resistivity, carrier concentration, and mobility have been supplemented by infrared reflectivity and transmissivity measurements. In addition, a contactless microwave method of measuring carrier concentration is being adapted for use with the films, a conventional high-voltage pulse technique has been used to study current density-vs-field characteristics, and a novel method of measuring high-field transport properties (employing a time-of-flight measurement in a specially designed transistor structure) is being developed for use on the heteroepitaxial films. (See Section II-2-f.)

The necessary design modifications in the AEI Model EM6 electron microscope to be used for the in situ observations of the nucleation and early-stage growth of CVD semiconductor films on insulating substrates are in progress. The instrument has been relocated into specially designed laboratories for this work. It is anticipated that tests of some of the auxiliary components and preliminary physical vapor deposition as well as simplified chemical reaction experiments will be carried out in the microscope during the second six months of the program. (See Section II-2-d.)

The preparative gas chromatograph to be used for the detailed analysis of the chemical reactants employed in CVD processes for semiconductor film deposition has been temporarily modified for higher sensitivity for these investigations. A sample handling system has been designed and is being assembled to facilitate transfer of the reactant samples from supply tanks to the chromatograph and to a mass spectrometer also to be used in the analyses. (See Section II-2-b.)

The preparation of polished wafers of both  $Al_2O_3$  and  $MgAl_2O_4$  to provide substrates for the Si and GaAs deposition experiments has been under way from the beginning of the contract year. A major improvement has been made in the procedure for polishing  $Al_2O_3$  substrates for (111) Si growth, using synthetic diamond dust (1  $\mu$ m particle size) in the final polishing step. A set of  $Al_2O_3$  substrate wafers has been selected for use in a series of analyses of the surface structure and impurity content in various stages of preparation for heteroepitaxial growth of semiconductor films. Techniques of Lang X-ray topography, scanning electron microscopy, low-energy electron diffraction, and Auger electron spectroscopy are to be utilized in these studies, in addition to conventional electron microscopy and electron diffraction analysis, X-ray diffraction analysis, and classical metallographic examination. (See Section II-2-c.)

An outline of plans for the second six months of the program is included. (See Section III.)

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13. ABSTRACT The objective of this program is to carry out a fundamental study of the nucleation and film growth mechanisms in heteroepitaxial semiconductor films and to apply the results to the preparation of improved thin films and thin-film devices on insulating substrates. The program involves both theoretical and experimental investigations. The emphasis is on chemical vapor deposition (CVD) technique. The Si-on $Al_2O_3$ and GaAs-on $Al_2O_3$ systems are emphasized but other semiconductors and other substrates, such as spinel and beryllia, are to be included. A generalized theoretical method for the study of crystallographic relationships between substrate and film has been developed, utilizing two-dimensional gaussian distributions of mass as replacements for real atoms on the substrate. The method, which allows pseudomorphic deformation to occur and accounts for the associated elastic strain energy, is applicable either to an extended film or to films of finite extent (i.e., islands). Another theoretical approach used, with particular attention to the interfacial cohesive and binding energies between film and substrate, involves a relatively short-range pairwise interatomic interaction potential between Si atoms and the Al and O atoms in and near the interface in the Si- $Al_2O_3$ system. Experimental studies of the effects of various growth parameters and other variables on the quality of Si film growth on $Al_2O_3$ and spinel substrates have been undertaken utilizing the pyrolysis of $SiH_4$ . The properties of nominally undoped Si films grown at temperatures less than 1050C are found to be dominated by surface conduction. N-type conductivity, with carrier concentrations from $\sim 10^{12}$ to $\sim 7 \times 10^{15} \text{ cm}^{-3}$ and mobilities as high as 700-850 $\text{cm}^2/\text{V-sec}$ are found, but properties vary greatly with surface conditions. Arsenic-doped n-type films with carrier concentrations from $10^{16}$ to $>10^{18} \text{ cm}^{-3}$ in both (111) and (100) orientations on $Al_2O_3$ have been prepared in both $H_2$ and He at temperatures as low as 950C with good electrical properties. Undoped Si films deposited at temperatures $>1050\text{C}$ are invariably p-type, due to autodoping. However, the exact role played by surface conduction is not yet fully evaluated. Chromatography studies designed to identify the impurities in reactants used in the deposition of Si and GaAs by CVD techniques, and preliminary studies and design of required modifications in an electron microscope to be used for <i>in situ</i> observation of semiconductor CVD are also under way. A novel method of measuring high-field transport properties based on a time-of-flight measurement has been developed. A detailed outline of the work planned for the second six months of the program is included.			